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(19)

(54) METHOD FOR THE SURFACE TREATMENT OF ARTICLES MADE FROM HYDROXYETHYL METHACRYLATE POLYMERS

(71) We, CESKOSLOVENSKA AKADEMIE VED, a Czechoslovakian corporation of No. 3 Národní, Praha 1, Czechoslovakia do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method for modifying the surfaces of articles formed from polymers containing free hydroxyl groups. More particularly, this invention relates to a method for modifying the surfaces of articles formed from an at least slightly cross-linked polymer or copolymer of hydroxyethyl methacrylate so as to increase the hydrophilic nature thereof and to the articles thereby obtained.

Hydrophilic polymers of the type containing hydroxyl groups either in the main or side chains thereof have assumed considerable practical importance, particularly in the cases where their tendency to undergo swelling in water has been reduced due to the effect of the carbon chains in the molecule to the point still permitting the realization of the desired mechanical properties. This technique for reducing swelling in water has been advantageously utilized for example, in connection with at least slightly cross-linked polymers of hydroxyethyl methacrylate. Such polymers even when only slightly cross-linked do not swell on exposure to water above about 45 volume per cent in water.

For various applications of the aforesaid type of polymers, as for instance in their use as biomedical materials, an improvement in their interaction with the surrounding living tissue would be realized if their hydrophilic character could be increased without any resultant detriment to their mechanical properties. This state can be obtained, heretofor only by the application of a surface layer of highly hydrophilic material onto the underlying polymeric structure, both the base and surface layers being adapted as nearly as possible to the single prupose of the required interaction with the medium in which the article is to be maintained. Thus, the base is required to be relatively low-swelling and thus of a mechanically tough material and the covering layer of a less tough, more readily swellable material. However, in order to avoid any unfavourable mechanical properties due to such covering layers, the same have had to be very thin and of course, provision has to be made so that they adhere perfectly to the base.

The experiments which have been carried out up until this time in this connection have involved the application of the highly hydrophilic layers to the base materials by means of soluble linear polymers and particularly by means of solutions of linear, non-cross-linked, hydroxyethyl methacrylate polymers. However, the adhesion of the films prepared in this manner has proved to be very unsatisfactory. Proposals in which it has been suggested to chemically graft the hydrophilic polymers onto free radicals created chemically or by radiation on the surface of the polymer article have proved somewhat more acceptable. However, this latter procedure has not been consistently successful and then only when considerable effort and expense have been involved in that it is almost impossible to prepare the thin layer of linear polymer and also the structure of the base is damaged with the grafting due to the penetration by the new chains through it in the polymerization of the strongly hydrophilic monomer so that the subsequent swelling does not only occur at the surface but to a considerable extent into the interior.

In accordance with the invention it has now been found that substantially hydrophilic layers can be formed at the surface of less hydrophilic at least slightly cross-linked polymers and copolymers of hydroxyethyl methacrylate, not by the application of an additional layer, but by a chemical conversion of the surface of the base polymer effected only to a relatively small depth.

According to the invention there is provided a method for the surface treatment of articles formed from an at least slightly cross-linked polymer or copolymer of hydroxyethyl methacrylate, which method comprises subjecting at least a portion of the surface of such an article to the action of a sulfonation or phosphorylation agent.

Thus in accordance with the invention, it has been found that the formation of a hydrophilic surface can be achieved by forming new highly hydrophilic groups on the already existing polymer chains which initially contain free hydroxyl groups of the alcoholic type particularly by esterifying such alcoholic groups with sulfuric or phosphoric acid thereby converting the alcohol groups to hydrogen ester groups, which can then be neutralized to form the corresponding alkali or other metallic or onium salts as follows:

$$\}—OH \rightarrow \}—O—SO_3H \rightarrow \}—O—SO_3^-Na^+$$

$$\}—OH \rightarrow \}—O—PO(OH)_2 \rightarrow \}—O—PO_2(OH)^-Na^+$$

The stability of the primary esters of sulfuric or phosphoric acid is entirely adequate even for long term application in aqueous medium, except in the case of the presence of mineral acids (for instance 1 N HCl) where the ester-linked sulfuric and phosphoric acid are rapidly split off.

The above set out substitution i.e. addition reaction can be carried out with any conventional agent used for direct or indirect sulfonation or phosphorylation of alcohol groups. The agents which have proved especially suitable include those having a rate of chemical conversion which is high in relation to the rate of their diffusion into the surface. In such cases, very thin and highly chemically converted surface layers are obtained with only a short exposure of the surface to the action of the agent. Suitable sulfonation agents include 60—100% sulphuric acid, fuming sulphuric acid, gaseous sulphur trioxide alone or mixed with a dry inert gas or gaseous sulphur trioxide dissolved in an organic solvent such as tetrachloro methane or dioxan. Also suitable are chlor-sulphuric and fluoro-sulphuric acids. Use of sulphur trioxide alone results in the formation of a superhydrophilic layer having a thickness of only 1 micron and surprisingly producing a change in the surface properties of the poly (hydroxyethyl methacrylate) hydrophilic gel, without in any way changing its mechanical properties or damaging the microscopic structure of the surface in any way.

Suitable phosphorylation agents include polyphosphoric acid, (especially when prepared from orthophosphoric acid and phosphorus pentoxide) and phosphoryl trichloride.

The process of the invention may be employed advantageously, for example in the superhydrophilization of soft hydrophilic contact lenses. This treatment results in there being obtained a superior sliding i.e., movement of the lens along the cornea. This movement favorably influences the tolerance and non-irritability of the lens. The considerable softness of the superhydrophilic layer is also advantageous in this connection.

If the agent which is selected for use, acts to swell the material of the base, as for instance, concentrated sulfuric acid or fluorosulfuric acid, mixtures of orthophosphoric acid and phosphorus pentoxide or dioxane solutions of sulfur trioxide, deeper layers are formed, for example, amounting to several tenths of a millimeter in thickness. These somewhat thicker layers are suitable for other specific applications because of the continuous transition from the maximally hydrophilized surface layer to the unchanged original material. A substantially perfect adhesion is achieved in this manner, since the internal stresses arising at the transition between layers of different swelling capacity are distributed uniformly throughout the entire volume of the modified layer.

The layers as realized in accordance with the invention differ expressly from a lamination of two different materials as taught by the art in that in the latter, the stresses are concentrated in the proximity of the boundary between the layers.

The procedure according to the invention is particularly adapted for use in the case where improved sliding of the articles is required, i.e., reduced friction as for instance in contact lenses, catheters, surgical sutures and in any application where injury to a living tissue or mucous membrane has to be prevented, packaging and protecting films and foils etc.

Before treatment with the sulphonation or phosphorylation agent, the surface to be treated may be previously impregnated with a compound containing a tertiary amine group, in particular pyridine.

The following examples are further illustrative of this invention, and it will be understood that the invention is not limited thereto.

EXAMPLE 1

A contact lens was manufactured by the conventional mechanical machining of a blank formed by a material comprising a copolymer prepared by polymerization of 12 parts by weight of butyl methacrylate, 87.7 parts by weight of hydroxyethyl methacrylate, and 0.3 parts by weight of ethyl dimethacrylate. Fol-

lowing final polishing to provide the desired optical quality and precise form of the edges, the central portion of the convex area of the lens was covered with paraffin in such a manner, that a border having a width of 1 mm remained uncovered. The lens was then attached by its paraffin covered central portion to a glass rod and, by means of this rod, immersed for 45 seconds into a vessel whose atmosphere was in equilibrium with fuming sulphuric acid containing 60% of sulphur trioxide. After this exposure, the lens was rinsed with water, freed of the paraffin by treatment with toluene, and equilibrated in a 1% solution of sodium bicarbonate. It could then be inserted and used as any other conventionally available contact lenses but it has the advantage of substantially friction and other interruption free movement of the lens area coming into contact with the cornea of the eye. The surface of the front portion of the lens is deliberately not subjected to sulfonation, as an improvement in its sliding movement would make removal of the lens more difficult.

Example 2

The catheter tube was manufactured by a known centrifugal casting method from slightly crosslinked poly(hydroxyethyl methacrylate). The catheter was coated in a dry state on its external surface with a syrupy mixture of polyphosphoric acid, which had been prepared from 3—5 parts of phosphorus pentoxide and 1—2 parts of orthophosphoric acid. The thereby coated catheter was then immersed into a bath of boiling hexane for 3 minutes. The catheter was thereafter rinsed with water, and stored in physiological saline solution diluted with half its volume of 1% aqueous bicarbonate. The catheter can be used directly following the sterilization thereof.

EXAMPLE 3

The exterior of a ship was coated according to known methods using a poly(hydroxyethyl methacrylate) varnish. The coating was then cured with potassium dichromate dissolved in varnish. Thereafter the coating was sulfonated at its surface by moving a vessel supplied with circulating dry air saturated with a mixture of sulfur trioxide vapors corresponding to warm (30°C) fuming sulfuric acid and 60% free SO_3 over the coated area. The exposure of the coating to the vapors amounted to an average of 30 to 60 seconds. As a result the hydrodynamic frictional resistance of the ship was decreased especially after strong swelling of the surface layer.

WHAT WE CLAIM IS:—

1. Method for the surface treatment of articles formed from an at least slightly crosslinked polymer or copolymer of hydroxyethyl methacrylate, which method comprises subjecting at least a portion of the surface of such an article to the action of a sulfonation or phosphorylation agent.
2. Method according to claim 1 wherein the sulfonation agent is 60—100% sulfuric acid.
3. Method according to claim 1 wherein the sulfonation agent is fuming sulfuric acid.
4. Method according to claim 1 wherein the sulfonation agent is gaseous sulfur trioxide.
5. Method according to claim 4 wherein the sulfonation agent is gaseous sulfur trioxide admixed with a dry inert gas.
6. Method according to claim 4 wherein the sulfonation agent is gaseous sulfur trioxide dissolved in an organic solvent.
7. Method according to claim 6 wherein said solvent is tetrachloromethane or dioxan.
8. Method according to claim 1 wherein said sulfonation agent is chlorosulfuric or fluorosulfuric acid.
9. Method according to claim 1 wherein said phosphorylation agent is polyphosphoric acid.
10. Method according to claim 9 wherein said polyphosphoric acid is prepared from orthophosphoric acid and phosphorus pentoxide.
11. Method according to claim 1 wherein said phosphorylation agent is phosphoryl trichloride.
12. Method according to claim 11 wherein the surface of said article has previously been impregnated with a compound containing a tertiary amine group.
13. Method according to claim 12 wherein the surface of said article has previously been impregnated with pyridine.
14. An article having at least a portion of its surface made more hydrophilic than the underlying base portion thereof, produced by the process of claim 1.
15. Method of surface treating articles made of polymers as claimed in claim 1 and substantially as described in any one of the examples herein disclosed.

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